



## **Notification of Acceptance of Manuscript**

Dear **N. A. Mansour, Nabil M. Hassan<sup>1</sup>, S.A. Abd Elaal, M. Fayez-Hassan, Mohamed Saad Seoud**

Paper ID **IJ16M0730**

Paper Title: **On the Comparison of Metals, Heavy and Toxics Elements in Waste Petroleum of Egypt and Kuwait**

**Volume: 3      Issue: 7      Month: July**

**Congratulations!** The review processes for “**On the Comparison of Metals, Heavy and Toxics Elements in Waste Petroleum of Egypt and Kuwait**” has been completed. The journal received submissions from various regions of country and institutions and outside country, which were reviewed by field experts and only some quality papers, have been selected for publication. Based on the recommendations of the reviewers and the Technical Experts, we are pleased to inform you that your paper identified above has been accepted for publication.

**Important:**

**In order to register the journal and get your paper included in the Journal successfully, you must finish following steps.**

1. Revise your paper according to the Review Comments provided in the attachment if any.
2. Download and complete the Copyright Form. [http://ijaetmas.com/wp-content/uploads/2014/07/IJAETMAS\\_Copyright.pdf](http://ijaetmas.com/wp-content/uploads/2014/07/IJAETMAS_Copyright.pdf)
3. The payment of registration fee should be done preferably by Cash Deposit/Net Banking. Completed copyright form along with payment receipt to be sent on the following Email Id: [editor.ijaetmas@gmail.com](mailto:editor.ijaetmas@gmail.com)

**If the above requirements are met by the set deadlines, the paper will be included in IJAETMAS Journal.**

Please strictly adhere to the format specified in the IJAETMAS template while preparing the final paper. For all the future communication please mention your Paper ID in subject line. In case of any problem, please feel free to contact us at [editor.ijaetmas@gmail.com](mailto:editor.ijaetmas@gmail.com) or [editor@ijaetmas.com](mailto:editor@ijaetmas.com). For the most updated information on the Issue, please check the Journal website at <http://www.ijaetmas.com/>. The Publication Schedule will be available at the website. Finally, we would like to further extend our congratulations to you and we are looking forward for more quality paper in IJAETMAS.

**Accounts Detail:**

**Payment Details:**

**Foreign Authors: 75 USD**

**Payment Method-1: Pay using PayPal, our Paypal Id is "[nusrat.sved@gmail.com](mailto:nusrat.sved@gmail.com)"**

**Payment Method-2: Pay Using Western Union Money Transfer to receiver**

**First Name : Syed**

**Last Name : Nusrat**

**Country : India City:**

**Ghaziabad**

***Yours sincerely,***

**Chief Editor,**

**IJAETMAS**

<http://www.ijaetmas.com/>

# On the Comparison of Metals, Heavy and Toxics Elements in Waste Petroleum of Egypt and Kuwait

N. A. Mansour<sup>1</sup>, Nabil M. Hassan<sup>1,2</sup>, S.A. Abd Elaal<sup>3</sup>, M. Fayed-Hassan<sup>4</sup> and Mohamed Saad Seoud<sup>1, 5</sup>

<sup>1</sup>Department of Physics, Faculty of Science, Zagazig University, Zagazig, P.O. Box 44519, Egypt

<sup>2</sup>Department of NORM Regulation, Korea Institute of Nuclear Safety (KINS), P.O. Box 114, Yusong, Daejeon 305-338, Republic of Korea

<sup>3</sup>Central Lab. for Elemental and Isotopic Analysis, N R C, EAEA, Egypt

<sup>4</sup>Department of Experimental Nuclear Physics, Nuclear Research Centre, EAEA, Egypt

<sup>5</sup>Calibration and Radiation Dosimetry Division, Radiation Protection Department, Ministry of Health, Kuwait

## Abstract

Petroleum waste of scale, sludge and sand that maintained various level of naturally occurring radioactive materials could also contain heavy and toxic elements which cause hazardous pollution to human health and the environment so that determination of these elements in waste petroleum samples are important to refineries, industrial processes, waste disposal and transports. Thus, the present work will focus on the evaluation the concentrations of metals, heavy and toxics elements in waste petroleum samples from petroleum companies located in Egypt and Kuwait using Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) and X-Ray Fluorescence (XRF) Techniques. 6 samples of scale, sludge and sand were collected, 3 samples from Kuwait petroleum companies and 3 samples from Egypt as well. More than 17 elements of metals, heavy elements and toxic metals of (Si, Cu, Al, S, K, Ca, Na, Mn, Fe, Zn, Pb, As, Br, Sr, Rh, Ba and Ti) were detected in the selected samples with various values. All the studied samples had high concentrations of Fe, K, Ca, S and Si rather than the other elements. The concentration of Iron in Egyptian samples was higher than in Kuwait samples whilst silicon and potassium were greater in Kuwait samples. All the other elements were almost same in Egyptian and Kuwait samples. Furthermore, the toxic element of barium was detected in Egyptian samples with high concentration but it was not detected in Kuwait samples (XRF). The two measurement methods show good agreement, No significant differences. The obtained results imply that the petroleum wastes need more monitoring in order to minimize the environmental pollution.

**Keywords:** Heavy and Toxic Elements, Metals, ICP-OES, XRF, Waste Petroleum Samples, Egypt, Kuwait.

## 1- Introduction

Petroleum industry is the main source of national income in Kuwait and important income source for Egypt also and many countries all over the world. At the same time it could cause negative impact to the environment and human health due to its waste. Several researchers reported that petroleum waste of scale, sludge and sand maintained various concentrations of naturally occurring radioactive materials (NORM) which increase radiation dose received to individual [1,2]. It could also contain different type of heavy and toxic elements with high concentrations [3]. Therefore measurement the concentration of heavy and toxic elements and metal is very important in order to decrease the environment pollution and to protect human health. Thus the present study will measure the concentration of those elements in waste petroleum samples collected from petroleum companies located in Egypt and Kuwait using Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) and X-Ray Fluorescence (XRF) Techniques.

It is easy to see why ICP-OES is such a robust technique for busy oil analysis laboratories. The ICP-OES method for the determination of additive elements, wear metals and contaminants in used oils as well as the determination of selected elements in base oils. X-ray fluorescence spectrometry (XRF) is also used for elemental determinations in oil. This application note compares the performance of ICP-OES with XRF for 5 elements (calcium, magnesium, phosphorus, sulfur and zinc) commonly determined by XRF. Oil analysis by XRF is very fast but limited in concentration range. ICP-OES has the concentration range necessary to determine additives, wear metals and contaminates in oils and can quickly determine the 22 elements suggest. Wear metals such as copper and iron may indicate wear in an engine or any oil-wetted compartment. Boron, silicon or sodium may indicate contamination from dirt or antifreeze leading to a failure. Additive elements such as calcium, phosphorus and zinc are analyzed for depletion which contributes to wear since these

elements contribute to certain key lubrication characteristics. A sound maintenance program which routinely measures metals in the lubricating oils not only reduces the expense of routinely dismantling the components for visual inspection, but can indicate unexpected wear before component failure. Element determination and quantification in liquid and solid petroleum samples is a topic of great interest in many fields. Usually, environmentally important elements are present at very low concentrations (trace and ultra-trace levels) and therefore the use of sensitive instrumental analytical techniques is mandatory.

Each of these techniques has its advantages and draw backs and thus, few laboratories rely only on one of these analytical methods but often use complementary combinations of them [4, 5]. This article gives an overview of the most commonly used analytical techniques of ICP-OES and XRF for element analysis of liquid and solid Petroleum samples in which the XRF technique can be used [6,7] to elemental determinations from sodium to uranium with concentration in the range of ppm. The most frequent form of sample preparation for XRF is the creation of pressed pellets. The XRF technique has the ability to handle wide variety of samples, including powders, liquids and solids [8, 9]. Special attention is given to current instrumentation and the advantages and limitations of each configuration mode are shown. One of the drawbacks of most Prodigy High Dispersion Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) for the Quantitative analysis of solid samples [10, 11] and have become popular in analytical laboratories owing to their versatility. In a few minutes, the (ICP-OES) can produce high quality data for elements with wide range of atomic masses, from  $^6\text{Li}$  to  $^{238}\text{U}$ . The best results are obtained for elements that have ionization potentials lower than those of the carrying gas (Ar, 15.8 eV) and that are free of isobaric interferences.

The most common applications for ICP-OES are in biological, environmental, geological, and industrial fields. .The analyses of samples were performed in the Central Laboratory for Elemental and Isotopic Analysis, Nuclear Research Center, Atomic Energy Authority. For elemental analysis of the

collected samples, the JMS PLASMA X2 High Resolution Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) was used for extremely low limits of detection (at microgram/nanogram per liter level) or isotopic analysis of different elements present in a sample is required, then ICP-OES systems are preferred. The unequivocal separation of analyze ions from spectral interferences is a prerequisite for accurate and precise elemental analysis when using such instrumentation [6, 12]. The potential use of ICP-OES for elemental and isotopic quantitative analyses was demonstrated early in the stage of its development (Hoefs, 1987) [13]. ICP-OES is used in a wide range of fields including earth sciences, medical applications, environmental studies, and in nuclear industry. The range and combination of elements, which can be analyzed by ICP-OES, is very broad.

The analytical tools used so far (ICP-OES) don't allow the analysis of the complete list, or in a reasonable analysis time that fits with routine analysis requirements. A rapid, sensitive, and multi-elemental method is then required to analyze trace elements occurring in crude oil or other petroleum products. Recently, ICP-OES was used to determine trace metals in petroleum samples, crude oils and their fractions (Dreyfus et al., 2005). In this study, an original method was developed that allowed direct determination of very low level trace elements in the range of few ppb. Sample throughput and multi-elemental capabilities are some common benefits of ICP-OES and compared to x-ray florescence technique (XRF). The inherent high sensitivity of ICP-OES detection together with isotopic ratio capabilities opens new fields of applications in petro chemistry or geochemistry of petroleum products. The combination of these two techniques thus provides a very wide concentration range of metal compounds to be determined on a routine basis, ICP-OES being preferred for major element analysis (Fe, Ni and V). However, these two techniques were not initially designed for organic samples analysis and specific configuration of sample introduction systems are required in order to minimize organic solvent load into the ICP plasma.

These techniques give sufficient detection limits for the common applications so, while the importance of metals in the products has not been ignored, not much attention has been given to updating analytical methods to take advantage of new technology such as ICP-OES. Papers published during these years have mainly discussed sample preparation such as emulsification [19], solvent extraction [20], and so on with XRF or ICP-OES. Although the superior sensitivity of ICP-OES is well known and ICP-OES is accepted in a variety of industrial fields, ICP-OES has not been widely utilized for routine applications in the petrochemical industry. There are various reasons for this, including the fact that petroleum manufacturing and refining sites do not require the superior sensitivity offered by ICP-OES. Another factor is that the high purity organic reagents needed for ultra-trace analysis are not commonly available in the commercial market. For example, metallic standards for petroleum samples analysis are manufactured by very few vendors. Although several elements can be determined by ICP-OES, the number of elements included in commercially available organic standards is around 30 at most. That number is sufficient for most existing methods, because the other elements are typically too low to be determined using ICP-OES. Regardless of the detection mode, analysis of petroleum samples presents a significant challenge for ICP instrumentation. It is very difficult to sustain an ICP when introducing organic solvents, particularly volatile ones. For ICP analysis, a liquid sample [21] is typically converted to an aerosol by an nebulizer; at the same time, a large amount of solvent vapor is created and transported to the ICP torch, even when a chilled spray chamber is used. Sample aerosol droplets and particles coming out of the central tube of the torch pass through the center of the plasma. However; organic vapor cannot do so because the high temperature argon plasma has a much higher viscosity than the low temperature organic vapor. If the linear velocity of the carrier gas is not high enough [22] to penetrate the plasma, the vapor surrounds the plasma and, as a result, cuts off the electromagnetic coupling between the load coil and ICP. The use of a narrower bore injector such as 1.0 mm internal diameter increases the linear gas velocity and allows the sample aerosol to punch

through the plasma, so enabling organic solvent introduction, but the sensitivity is reduced by approximately 30% compared to a typical injector used with aqueous samples. For analysis by ICP-OES, the high concentration of carbon matrix in the organic samples could [23] also lead to soot deposits on the sampling cone and torch. In order to avoid such deposits, ICP-OES requires the addition of O<sub>2</sub> to the carrier gas to decompose the carbon in the plasma. In order to ignite the ICP with O<sub>2</sub> gas present, a very robust radio frequency (RF) generator circuit is required. Successful analysis of petroleum samples using ICP-OES must overcome these challenges. The all solid state RF generator for the Agilent 7700 series ICP-OES is so robust that a 1.5 mm injector torch can be used to introduce most organic solvents. Moreover, the ignition of the ICP is possible with organic solvent and oxygen [24] present. These applications note compares the performance of ICP-OES with XRF for all elements (Si, P, S, K, Ca, Mn, Fe, Zn, As, Br, Rh, Ba, Ho, Ti) commonly determined by XRF. Wear metals[25] such as copper and iron may indicate wear in an engine or any petroleum oil Samples wetted compartment. Boron, silicon or sodium may indicate contamination from dirt or antifreeze leading to a failure. Additive elements such as calcium, phosphorus and zinc are analyzed for depletion which contributes to [26] wear since these elements contribute to certain key lubrication characteristics. It is easy to see why ICP-OES is such a robust technique for busy petroleum samples analysis laboratories. This question is addressed in this work using ICP-OES and hand-held XRF to examine a variety of petroleum samples. Ease of [27] use and agreement between techniques at the current level for all elements were evaluated [28].

## **2- Experimental apparatus:**

6 samples of scale, sludge and sand were collected from petroleum companies located in Egypt and Kuwait. Then the samples were dried in oven at 110 °C for 24 h. The they were sieved and

chemically prepared for measurements. The samples were measured using Prodigy High Dispersion Inductively Coupled Plasma Optical Emission Spectrometer (Teledyne Leeman ICP-OES USA) and X-Ray Fluorescence Technique (XRF) figure 1,2 at Central Laboratory for Elemental and Isotopic Analysis, Nuclear Research Center, Egyptian Atomic Energy Authority, Cairo, Egypt, under the operational conditions of ICP- OES as shown in Table 1.

### **3-Results and Discussion:**

The analysis of scale, sludge and sand samples by hand-held XRF and ICP-OES are shown in Tables 2-7. The check mark in the XRF column indicates the XRF analysis displayed a lead value higher than the limit of 600 mg/kg in the screened toy indicating further quantitative analysis is recommended. The value determined by ICP-OES confirms that the value was higher than the regulatory limit in the coating or for a total analysis of the substrate material.



**Fig. (1) The Teledyne Leman ICP-OES.**

**Table (1): Show the operational conditions of ICP- OES.**

| ICP Spectrometer              | Leeman Prodigy Prism ICP-OES (USA) |
|-------------------------------|------------------------------------|
| RF Power                      | 1.2KW                              |
| Coolant gas flow              | 20 L/min                           |
| Auxiliary gas flow            | 0.3 L/min                          |
| Nebulizer gas flow            | 36 psi                             |
| Solution Uptake Rate          | 1 mL/min                           |
| Mg II/Mg I Ratio (Robustness) | 6                                  |
| Replicates                    | 3                                  |
| Integration time              | 10 Sec.                            |



**Fig. (2) XRF technique set up.**

Tables 2-7 show the results for selected samples analysis of three different types of samples. It is interesting to note the lead level is high, in agreement with the XRF analysis. Several other elements, such as chromium, are also high. The XRF value reported for Zn was 0.1239 mg/kg (Table 2). Regulations are continually changing and may require different elements to be monitored in the future, at different concentration levels [29]. One way to help in preparing for that eventuality is the use of the universal data acquisition (UDA) feature, exclusive to the Optima ICP-OES software. In this case the

Optima ICP-OES collects data for all of the wavelengths all of the time. If a standard is run at the time of the original data acquisition that includes more elements than the elements of interest at that moment, other elements can be measured with good quantitative accuracy by reprocessing at a later date. If an elemental concentration is of interest for an element that was not included in any of the usual multi-element [30] standards, reprocessing can provide a semiquantitative result, usually within  $\pm 30\%$  of the true value. Both the original set of elements reported and the elements determined later by reprocessing the data to examine the information previously stored for those elements are listed. This can be useful in petroleum samples that may have been disposed or in better understanding the scope of petroleum samples in preparing for future analyses.

This work presents an analysis of macro and micro element maintains in petroleum samples in a comparison with the newest literature data. Calcium contents of the petroleum samples varied in most of the studies between 0.9 - 1.02 mg/kg. Average Mn concentration of the petroleum samples was 0.25 - 0.28 mg/kg, Ca contents of the petroleum samples is from 14.01-15.83 mg/kg, potassium contents from 12.30 - 26.15 mg/kg. Iron contents of petroleum samples were found in extreme cases between 5.71 - 172 mg/kg (agreed with XRF results) illustrated in figures 3-7, which is not affected by the environment, the iron intake and the contraceptive preparations. S contents of the petroleum samples vary between 13.14 - 10.58 mg/kg. The effect of analysis on the as contents is controversial, and it appears that the as contents are not influenced by either the nutrient or the as intake. Br contents of the petroleum samples were measured to be between 0.29–0.57 mg/kg, it is difficult to specify an average value due to variations of order of magnitude. Similarly, there are extreme values obtained for the Sr contents 0.51 - 0.61 mg/kg, which can be explained by the different Sr intake of the petroleum samples, or by extreme Sr burden of the environment. Out of the other micro elements, we analyze the nickel, cobalt, barium, selenium, hafnium and silicon maintained in petroleum samples, while among all toxic trace elements, we focus on the concentration of cadmium, lead, mercury and barium in petroleum samples as given in Tables 2-7. Amount of latter ones in the petroleum samples is affected by contaminated the polluted urban air; exhaust gas of the motor vehicles, the polluted environment. Holmium contents of the petroleum samples were measured to be 0.15 mg/kg. Barium, beryllium, bismuth, cadmium, cesium, lanthanum, lithium, rubidium, antimony, tin, strontium, thallium content was determined. It was established that concentration of such toxic elements like

barium, beryllium, and lithium was considerably higher, and it appears that bismuth, strontium does not change. Concentration of barium, cesium, and strontium decreases the suckling, which can mean even a difference of 60%, which that must be taken into consideration when collecting the petroleum samples. Also in this study we determined toxic element of transitional aluminum and arsenic. The aluminum concentration was measured to be 1.26 - 37.22 mg/kg, and arsenic concentration to be 0.02 - 1.06 mg/kg. Coni et al. [29] analyzed some trace elements.

For the petroleum waste samples the following trace element concentrations were obtained: barium, bismuth, lithium, strontium, and thallium. Beyond determination of the micro elements it was also examined the materials of interest were linked in the petroleum samples. Wappelhorst et al. [30] determined cerium, gallium, lanthanum, niobium, ruthenium, silver, thorium, titanium and uranium content of petroleum samples and examined. Based on micro element content of the petroleum samples, it was calculated in what ratio the micro element present in the petroleum samples. The calculated transfer factor for silver was 5.1, for cerium 16.1, for gallium 19.1, for lanthanum 13.8, for niobium 20.7, ruthenium 4.1, for antimony 13.2, for thorium 20.2, for titanium 5.6, and for uranium 21.3. The transfer factors significantly differed from each other in case of the individuals. These differences were explained by the differences in the petroleum samples production. Average silver content of the petroleum samples was measured to be 0.33  $\mu\text{g}/\text{kg}$ , cerium content to be 0.03  $\mu\text{g}/\text{kg}$ , gallium content to be 0.03  $\mu\text{g}/\text{kg}$ , lanthanum content to be 0.04  $\mu\text{g}/\text{kg}$ , niobium content to be 0.02  $\mu\text{g}/\text{kg}$ , ruthenium content 0.18  $\mu\text{g}/\text{kg}$ , antimony content to be 0.04  $\mu\text{g}/\text{kg}$ , thorium content to be 0.03  $\mu\text{g}/\text{kg}$ , titanium content to be 0.08  $\mu\text{g}/\text{kg}$  and radium content to be 0.02  $\mu\text{g}/\text{kg}$ . Arsenic content of petroleum samples was 0.9  $\mu\text{g}/\text{dm}^3$  and that of petroleum samples was 5.2  $\mu\text{g}/\text{dm}^3$ . Toxic elements in petroleum samples raise the important issues for pediatric practice, for the practice of public health, and for the environmental health research community. There is insufficient information on the nature and levels of contaminants in petroleum samples. Feasible analytical methods are now available for lead and cadmium in petroleum samples and in this research line, exposure to other toxic metals from different sources, can also be able to be measured in petroleum samples. The results of this study will lead into the consideration of chemicals in petroleum samples as an invaluable tool in environmental risk assessment.

Table 2 : Analysis of sludge, scale and sand samples using XRF technique

| XRF Technique |               |              |            |
|---------------|---------------|--------------|------------|
| Egypt (%)     |               |              |            |
| Element       | Sludge (ESL5) | Scale (ESc1) | Sand (ES1) |
| Si            | 1.35          | 2.36         | 47.62      |
| P             | 3.43          | ND           | 0.47       |
| S             | 13.14         | 6.27         | 2.38       |
| K             | 12.30         | 0.20         | 1.48       |
| Ca            | 14.01         | 4.56         | 15.74      |
| Mn            | 0.25          | 0.31         | ND         |
| Fe            | 52.05         | 79.52        | 12.18      |
| Zn            | 0.12          | 0.11         | 0.10       |
| As            | 0.07          | ND           | ND         |
| Br            | 0.29          | ND           | ND         |
| Sr            | 0.51          | 1.46         | 0.33       |
| Rh            | ND            | ND           | ND         |
| Ba            | 2.33          | 5.23         | 18.02      |
| Ho            | 0.15          | ND           | ND         |
| Ti            | ND            | ND           | ND         |

| Kuwait (%) |               |              |            |
|------------|---------------|--------------|------------|
| Element    | Sludge (KSL1) | Scale (KSc1) | Sand (KS2) |
| Si         | 1.07          | 4.44         | 45.70      |
| P          | 6.70          | ND           | ND         |
| S          | 10.58         | 27.53        | 13.12      |
| K          | 26.15         | 0.57         | 6.40       |
| Ca         | 15.83         | 6.50         | 20.36      |
| Mn         | 0.28          | 1.05         | 0.12       |
| Fe         | 38.07         | 58.65        | 7.53       |
| Zn         | ND            | 0.11         | ND         |
| As         | ND            | ND           | ND         |
| Br         | 0.57          | ND           | ND         |
| Sr         | 0.61          | 0.10         | 0.24       |
| Rh         | ND            | ND           | 0.04       |
| Ba         | ND            | ND           | ND         |
| Ho         | ND            | 0.33         | ND         |
| Ti         | 0.15          | 0.11         | 0.85       |

ND : not-detected

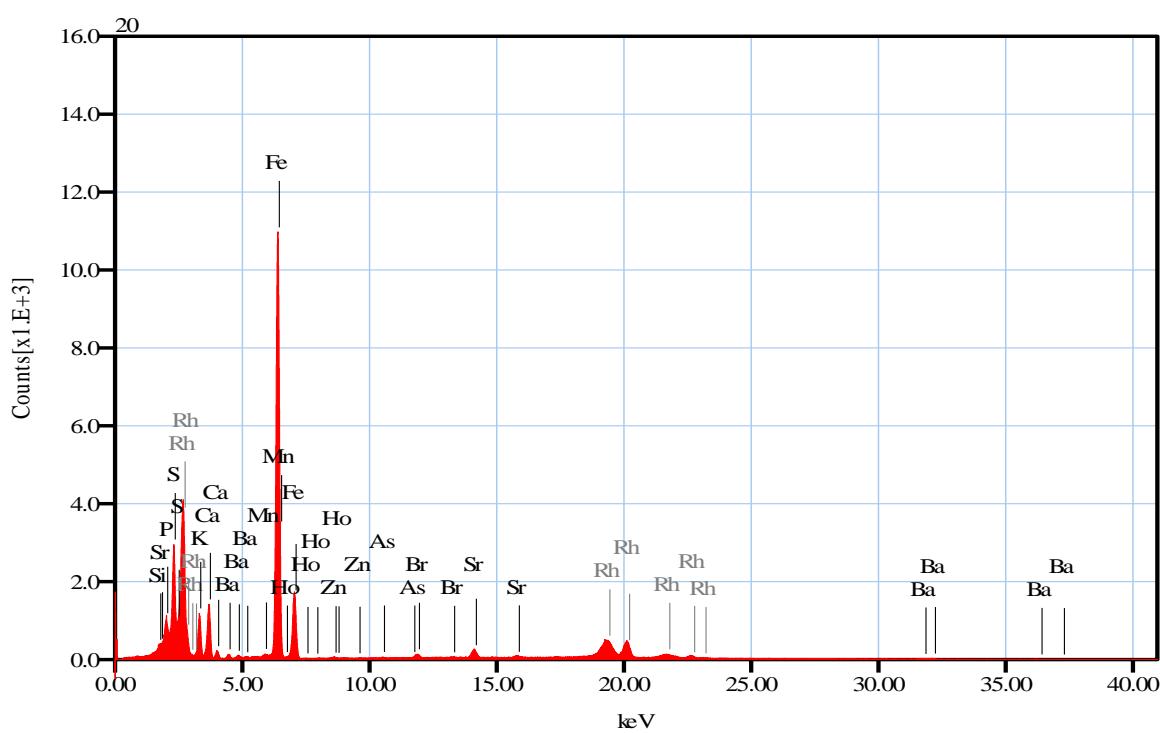
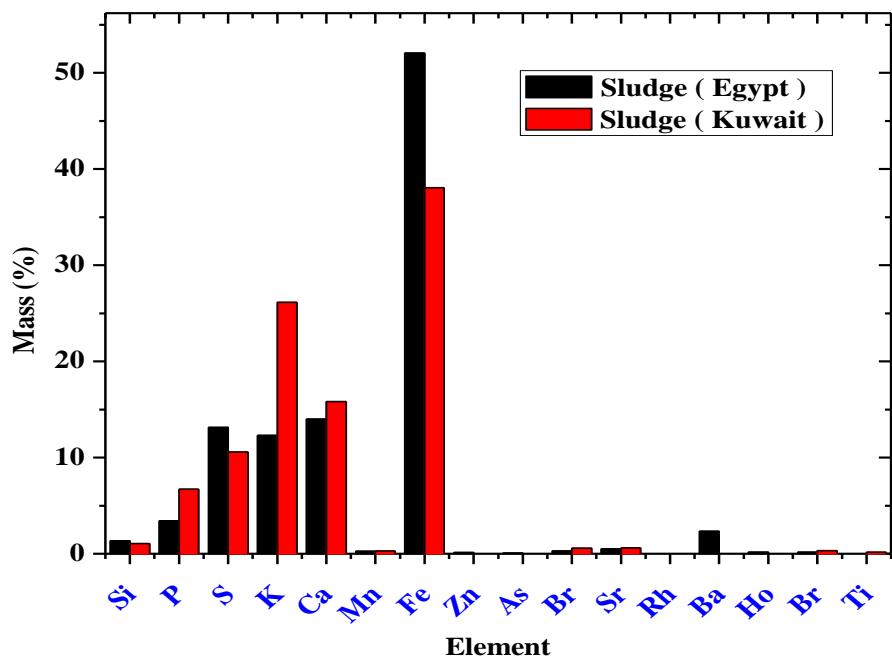
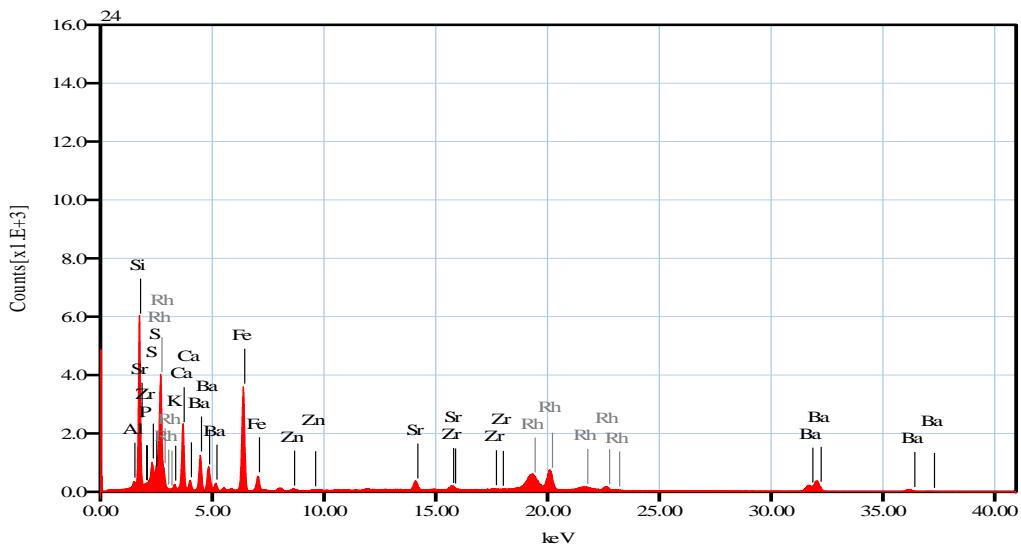


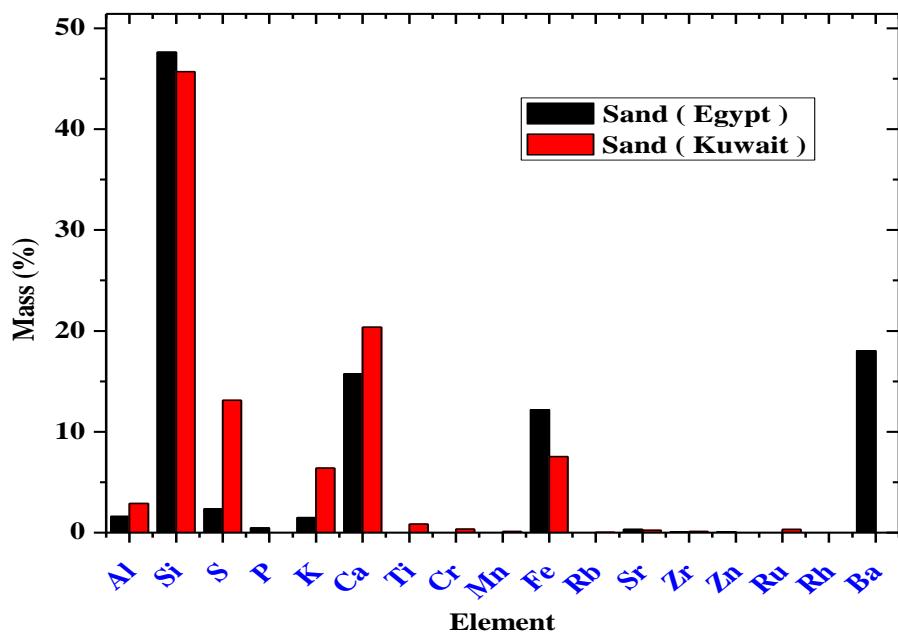
Fig. (3): Spectrum of the Sludge (Egypt) Sample Code (ESL5) analyzed by the XRF Technique



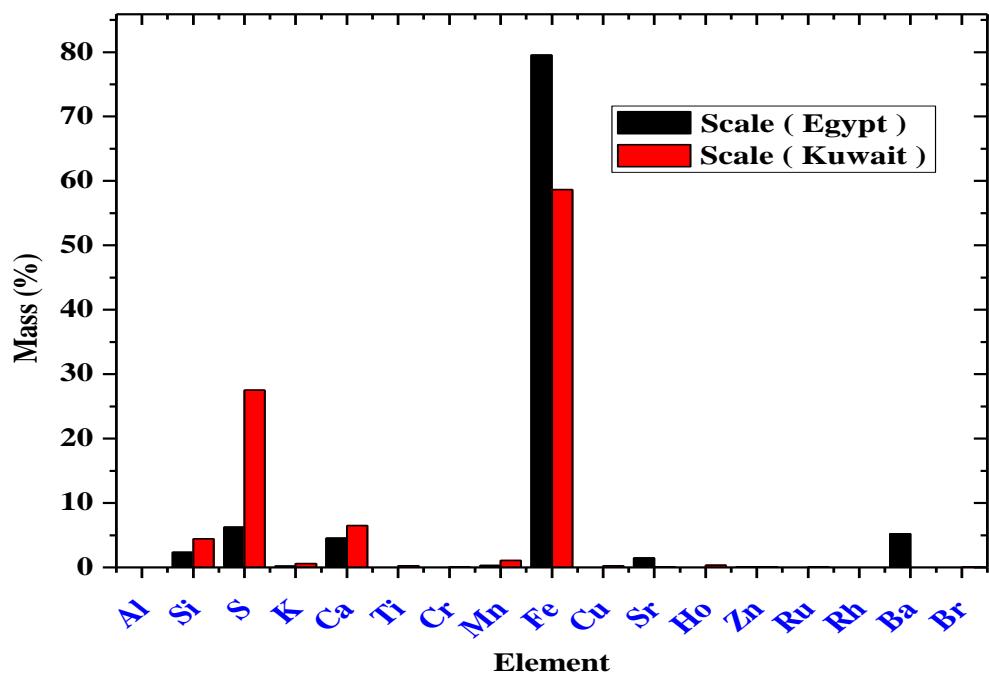
**Fig. (4) Analysis of the Sludge Samples Code (ESL5) & (KSL1) Using XRF Technique.**



**Fig. (5): Spectrum of the Sand around oil well (Egypt) Sample Code (ES1) analyzed by The XRF Technique**



**Fig. (6) Analysis of the Sand Samples Code (ES1) & (KS2) Using XRF Technique.**



**Fig. (7) Analysis of the Scale Samples Code (ESc1) & (KSc1) Using XRF Technique.**

**Table (3) ICP-OES Technique Results**

| ICP-OES Technique |          |                  |       |
|-------------------|----------|------------------|-------|
| (ESc1)            |          | (KSc1)           |       |
| Scale ( Egypt )   |          | Scale ( Kuwait ) |       |
| Element           | ppm      | Element          | Ppm   |
| As 189.042        | ND       | As 189.042       | ND    |
| Cd 214.441        | 58.44    | Cd 214.441       | 16.50 |
| Cs 894.347        | ND       | Cs 894.347       | ND    |
| Pb 220.353        | 1102.74  | Pb 220.353       | 311.1 |
| Se 196.090        | ND       | Se 196.090       | ND    |
| Ag 328.068        | ND       | Ag 328.068       | ND    |
| Sr 407.771        | 1098.9   | Sr 407.771       | 84    |
| Zn 213.856        | 194.04   | Zn 213.856       | 66    |
| Cu 224.700        | 455.28   | Cu 224.700       | 203.2 |
| Cr 205.552        | 362.37   | Cr 205.552       | 778.8 |
| Al 396.152        | 524.43   | Al 396.152       | 11525 |
| V 292.401         | 140.67   | V 292.401        | 41.7  |
| Na 588.995        | 21427.11 | Na 588.995       | 13652 |
| K 766.491         | 3030.81  | K 766.491        | 11742 |
| Ca 393.366        | 3298.11  | Ca 393.366       | 7925  |
| Mg 279.553        | 1305.66  | Mg 279.553       | 1855  |
| Fe 259.940        | 72472.5  | Fe 259.940       | 56890 |
| Ni 231.604        | ND       | Ni 231.604       | ND    |
| Mn 257.610        | 876.84   | Mn 257.610       | 1158  |
| Ba 455.403        | 2399.28  | Ba 455.403       | 80    |
| Co 228.615        | 31.23    | Co 228.615       | 12.72 |
| Zr 339.198        | ND       | Zr 339.198       | ND    |
| Mo 202.030        | 6.45     | Mo 202.030       | 0.24  |
| Ce 413.765        | ND       | Ce 413.765       | ND    |
| Eu 381.967        | ND       | Eu 381.967       | ND    |
| Gd 342.247        | 200.9    | Gd 342.247       | 105.9 |
| Lu 261.542        | 3.840    | Lu 261.542       | ND    |
| Nd 430.358        | ND       | Nd 430.358       | ND    |
| Si251.611         | 6724.17  | Si251.611        | 5749  |
| La333.749         | 14.340   | La333.749        | 9.300 |
| Sm 359.260        | 4.350    | Sm 359.260       | ND    |
| Tm 313.126        | ND       | Tm 313.126       | ND    |
| Er 337.271        | 89.0     | Er 337.271       | 553.8 |

**Table (4) ICP-OES Technique Results**

| ICP-OES Technique |        |                 |         |
|-------------------|--------|-----------------|---------|
| (ES1)             |        | (KS2)           |         |
| Sand ( Egypt )    |        | Sand ( Kuwait ) |         |
| Element           | ppm    | Element         | ppm     |
| As 189.042        | ND     | As 189.042      | 3.39    |
| Cd 214.441        | ND     | Cd 214.441      | ND      |
| Cs 894.347        | ND     | Cs 894.347      | 9.27    |
| Pb 220.353        | 190.3  | Pb 220.353      | 10.65   |
| Se 196.090        | ND     | Se 196.090      | 16.37   |
| Ag 328.068        | ND     | Ag 328.068      | ND      |
| Sr 407.771        | 336    | Sr 407.771      | 69.27   |
| Zn 213.856        | 102    | Zn 213.856      | 93.15   |
| Cu 224.700        | 53.1   | Cu 224.700      | ND      |
| Cr 205.552        | 788.5  | Cr 205.552      | 7.98    |
| Al 396.152        | 7763   | Al 396.152      | 9969.35 |
| V 292.401         | 9.6    | V 292.401       | 16.45   |
| Na 588.995        | 12714  | Na 588.995      | 5077.66 |
| K 766.491         | 9571   | K 766.491       | 6964.19 |
| Ca 393.366        | 18808  | Ca 393.366      | 4279.11 |
| Mg 279.553        | 1719   | Mg 279.553      | 2072.34 |
| Fe 259.940        | 11934  | Fe 259.940      | 3328.23 |
| Ni 231.604        | ND     | Ni 231.604      | 1.85    |
| Mn 257.610        | 164    | Mn 257.610      | 83.63   |
| Ba 455.403        | 2815   | Ba 455.403      | 956.05  |
| Co 228.615        | 17.88  | Co 228.615      | ND      |
| Zr 339.198        | 30.84  | Zr 339.198      | 150.40  |
| Mo 202.030        | 17.07  | Mo 202.030      | 42.50   |
| Ce 413.765        | ND     | Ce 413.765      | ND      |
| Eu 381.967        | 15.510 | Eu 381.967      | ND      |
| Gd 342.247        | 35.1   | Gd 342.247      | ND      |
| Lu 261.542        | ND     | Lu 261.542      | ND      |
| Nd 430.358        | ND     | Nd 430.358      | ND      |
| Si251.611         | 7838   | Si251.611       | ND      |
| La333.749         | 3.450  | La333.749       | ND      |
| Sm 359.260        | ND     | Sm 359.260      | ND      |
| Tm 313.126        | 8.850  | Tm 313.126      | ND      |
| Er 337.271        | 569.2  | Er 337.271      | ND      |

**Table (5) ICP-OES Technique Results**

| ICP-OES Technique |          |                   |          |
|-------------------|----------|-------------------|----------|
| (ESL5)            |          | (KSL1)            |          |
| Sludge ( Egypt )  |          | Sludge ( Kuwait ) |          |
| Element           | ppm      | Element           | Ppm      |
| As 189.042        | ND       | As 189.042        | 0.89     |
| Cd 214.441        | ND       | Cd 214.441        | ND       |
| Cs 894.347        | 3.15     | Cs 894.347        | 5.40     |
| Pb 220.353        | 38.31    | Pb 220.353        | 2.02     |
| Se 196.090        | ND       | Se 196.090        | ND       |
| Ag 328.068        | ND       | Ag 328.068        | 7.82     |
| Sr 407.771        | 378.79   | Sr 407.771        | 242.90   |
| Zn 213.856        | 382.10   | Zn 213.856        | 164.11   |
| Cu 224.700        | 23.63    | Cu 224.700        | 5.08     |
| Cr 205.552        | 48.06    | Cr 205.552        | 29.27    |
| Al 396.152        | 5688.79  | Al 396.152        | 1610.40  |
| V 292.401         | 41.61    | V 292.401         | 40.32    |
| Na 588.995        | 18927.90 | Na 588.995        | 20016.45 |
| K 766.491         | 52564.44 | K 766.491         | 63780.40 |
| Ca 393.366        | 2656.13  | Ca 393.366        | 2873.87  |
| Mg 279.553        | 1113.95  | Mg 279.553        | 740.56   |
| Fe 259.940        | 30950.56 | Fe 259.940        | 27868.63 |
| Ni 231.604        | 11.13    | Ni 231.604        | 4.60     |
| Mn 257.610        | 390.89   | Mn 257.610        | 324.92   |
| Ba 455.403        | 1465.16  | Ba 455.403        | 92.74    |
| Co 228.615        | ND       | Co 228.615        | ND       |
| Zr 339.198        | 20.32    | Zr 339.198        | 96.13    |
| Mo 202.030        | 26.69    | Mo 202.030        | 73.79    |
| Ce 413.765        | ND       | Ce 413.765        | ND       |
| Eu 381.967        | ND       | Eu 381.967        | ND       |
| Gd 342.247        | ND       | Gd 342.247        | ND       |
| Lu 261.542        | ND       | Lu 261.542        | ND       |
| Nd 430.358        | 193.71   | Nd 430.358        | 114.35   |

**Table(6) ICP-OES Technique Results**

| Sample Type | Sample Code | Analytes  | Detector |
|-------------|-------------|---|----------|
| Scale       | ESc1        | Cd, Pb, Sr, Zn, Cu, Cr, Al, V, Na, K, Ca, Mg, Fe, Mn, Ba, Co, Mo, Gd, Lu, Si, La, Sm, Er.                 | ICP-OES  |
|             | KSc1        |   |          |
| Sludge      | ESL5        | As, Cd, Cs, Pb, Ag, Sr, Zn, Cu, Cr, Al, V, Na, K, Ca, Mg, Fe, Ni, Mn, Ba, Zr, Mo, Nd.                     | ICP-OES  |
|             | KSL1        |   |          |
| Sand        | ES1         | As, Cs, Pb, Se, Sr, Zn, Cu, Cr, Al, V, Na, K, Ca, Mg, Fe, Ni, Mn, Ba, Co, Zr, Mo, Eu, Gd, Si, La, Tm, Er. | ICP-OES  |
|             | KS2         |   |          |

**Table (7) XRF TechniqueResults**

| Sample Type | Sample Code | Analytes   | Detector |
|-------------|-------------|--|----------|
| Scale       | ESc1        | Si, S, K, Ca, Ti, Cr, Mn, Fe, Cu, Sr, Ho, Zn, Ru, Ba, Br.    | XRF      |
|             | KSc1        |  |          |
| Sludge      | ESL5        | Si, P, S, K, Ca, Mn, Fe, Zn, As, Br, Sr, Ba, Ho, Ti.         | XRF      |
|             | KSL1        |  |          |
| Sand        | ES1         | Al, Si, S, P, K, Ca, Ti, Cr, Mn, Fe, Rb, Sr, Zr, Zn, Ru, Ba. | XRF      |
|             | KS2         |  |          |

## **Conclusion:**

Heavy and toxic elements and metals maintained in waste petroleum samples of scale, sludge and sand collected from Egyptian and Kuwait petroleum companies were measured using XRF and ICP-OES techniques. XRF provides rapid screening with a high degree of confidence and ICP-OES confirms the evaluation of elements concentration with highly accuracy. ICP-OES analysis shows good agreement with X-ray fluorescence spectroscopy on the high concentration elements. More than 17 elements of metals, heavy and toxic elements of (Si, Cu, Al, S, K, Ca, Na, Mn, Fe, Zn, Pb, As, Br, Sr, Rh, Ba and Ti) were detected in the studied samples. The major elements of Fe, Si, Ca, K, S, P and Ba were detected with various concentrations in sludge, scale and sand samples. It was notice that Fe concentration was higher in Egyptian samples than in Kuwait sample while the other elements were higher in Kuwait samples. Nevertheless, toxic element of barium was detected in Egyptian samples with high concentration of 18.02% but it was not detected in Kuwait samples (XFR). These results high light the importance of monitoring the waste petroleum samples of scale sludge and sand to minimize the hazardous to human health and environmental pollution.

## **5-References**

- 1- Abo-Elmagd M, Soliman HA, Daif MM (2009) Radon effective dose from TENORMwaste associated with petroleum industries. *Radiat Prot Dosim* 136: 209-215.
- 2-Al-Attar L., Safia B. and Abdul-Ghani B., (2016) Chemical composition of scales generated from oil industry and correlation to radionuclide contents and gamma-ray measurements of  $^{210}\text{Pb}$ . *Journal of Environmental Pollution* 210, 246 – 252.
- 3- Obiajunwa E. I., Pelemo D. A., Owolabi S. A. and Fasasi M. K., (2002) Characterisation of heavy metal pollutants of soils and sediments around a crude-oil production terminal using EDXRF. *Nuclear Instruments and Methods in Physics Research B* 194, 61–64.
- 4- Cember, H., (1985): "Introduction to health physics"Northwestern University.
- 5- Cooper, J. R., Randle, K., and Sokhi, R.S., (2003): "Radioactive Releases in the Environment: Impact andAssessment. John Wiley & Sons, Ltd, the Atrium, Southern Gate, hichester, West Sussex PO19 8SQ, England].
- 6- Bioar Khansa, (2005): "Petroleum, Its importance, Its risks and Challenges".
- 7- Egyptian Ministry of Petroleum Ministry Achievements, 2013.
- 8- Henriksen, T., and Maillie, H.D., (2003) :"Radiation and health", Taylor & Francis, Inc., New York.
- 9- H.R. Verma,(2007): "Atomic and Nuclear Analytical Methods" VerlagBerlin Heidelberg, New York.

10- ICRP, (2007): "The 2007 Recommendations of the International Commission on Radiological Protection". ICRP Publication 103. Ann. ICRP 37 (96).

11- Krieger, R., (1981): "Radioactivity of construction materials", Betonwerk. Fertigteil-Technol. 47, 468.

12- Reilly, T.D., Ensslin, N., Smith, H.A., Jr., and Kreiner, S., (1991): "Passive Nondestructive Assay of Nuclear Materials". Los Aalmos National Laboratory, United States Nuclear Regulatory Commission, NUREG/CR-5550, LAUR- 90-732, and Washington DC-USA].

13- State of Kuwait Ministry Of Oil- Petroleum Information, 2013.

14- Speight JG. Handbook of petroleum product analysis. New Jersey: John Wiley& Sons Inc; 2002.

15- Gary JH, Handwerk GE, Kaiser MJ. Petroleum refining: technology and economics. 5th ed. Boca Raton: CRC Press; 2007.

16- Stanislaus A, Marafi A, Rana MS. Recent advances in the science and technologyof ultra-low sulfur diesel (ULSD) production. Catal Today 2010; 153:1-68.

17- Corro G. Sulfur impact on diesel emission control, a review. React KinetCatal Lett 2002; 75:89-106.

18- Sydbom A, Blomberg A, Parnia S, Stenfors N, Sandstrom T, Dahlen SE. Health effects of diesel exhaust emissions. Eur Respire J 2001; 17:733-46.

19- McDonald JD, Harrod KS, Seagrave J, Seilkop SK, Mauderly JL. Effects of low sulfur fuel and a catalyzed particle trap on the composition and toxicity of diesel emissions. Environ Health Perspect 2004; 112:1307-12.

20- Yin C, Li H, Liu H, Zhao L, Bai Z, Wang Y, et al. Study on the formation, determination, and removal of elemental sulfur in ultra-low sulfur gas oil. Fuel Process Technol 2014; 120:16-21.

21- Wang FC-Y, Robbins WK, Di Sanzo FP, McElroy FC. Speciation of Sulfur containing compounds in diesel by comprehensive two-dimensional gas Chromatography. J Chromatogr Sci 2003; 41:519-23.

22- EPA, Environmental Protection Agency. Heavy-duty engine and vehicle standards and highway diesel fuel sulfur control requirements. United States, United States; 2000.

23- Directive 98/70/EC of the European Parliament and of the Council Official Journal of the European Union, EU, Relating to the quality of petrol and diesel fuels and amending, Council Directive 93/12/EEC. In: European Union; 1998. p. 174-88.

24- J. R. de Souza, E. F. dos Santos, C. B. Duyck and T. D. Saint'Pierre, Spectrochim. Acta, Part B, 66, 368-372 (2011).

25- ASTM D3237-12, Standard Test Method for Lead in Gasoline by Atomic Absorption Spectroscopy, originally approved in 1973, currently approved in 2012.

26- ASTM D4628-05, Standard Test Method for Analysis of Barium, Calcium, Magnesium and Zinc in Unused Lubricating Oils by Atomic Absorption Spectrometry, originally approved in 1986, currently approved in 2011.

27- ASTM D5863-00a, Standard Test Methods for Determination of Nickel, Vanadium, Iron and in Crude Oils and Residual Fuels by Flame Atomic Absorption Spectrometry, originally approved in 1995, currently approved in 2011.

28- ASTM D5185-09, Standard Test Method for Determination of Additive elements, Wear Metals, and Contaminants in Used Lubricating Oils, originally approved in 1991, urrently approved in 2009].

29- ASTM D7111-11, Standard Test Method for Determination of Trace Elements in Middle Distillate Fuels, approved in 2005. 7. D. M. Brum, C. F. Lima, N. F. Robaina, T. C. O. Fonseca and R. J. Cassella, Spectrochim. Acta, Part B, 66, 338-344 (2011).

30- M. Rahmani and M. Kaykhaii, Microchim. Acta, 174, 413-419 (2011).